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Chemistry and Mineralogy of Samples from the
Strategic Petroleum Reserve Bryan Mound Site

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ABSTRACT

Samples of Bryan Mound salt cores, sidewall samples and drill cuttings have been subjected to chemical, mineralogical and petrographic analysis. Halite $(NaCl)$ was the major mineral in all samples with anhydrite $(CaSO_4)$ a common accessory. Minor or trace sylvite (KCl) and quartz (SiO_2) were detected in some sidewall samples. Other minor minerals found in drill cuttings included quartz; mixed carbonates of Fe, Ca and Mg; and several iron oxides. Possibly the carbonates are reaction products with the basic drilling mud or possibly pieces of caprock which contaminated the cuttings. The iron oxides were probably produced by corrosion of the drill stem or bit.

Examination of thin sections made from pieces of core showed that anhydrite crystals were distributed through the halite grains and not concentrated at halite grain boundaries. Dark veins observed in some sections of core are anhydrite rich. The relative amount and distribution of anhydrite in the salt could be important to the mechanical properties of the bulk salt.

Samples of core were dissolved in water and the insoluble residues collected. Only anhydrite was found in the residues. The brines produced by dissolving the cores were analyzed for Na^+, K^+, Ca^{++}, Cl^-, $SO_4^=$ and several other ions. Equivalent amounts of Ca^{++} and $SO_4^=$ were found in each solution indicating these ions were the result of dissolution of some of the anhydrite from the original samples. The fraction of the original anhydrite that dis-

solved **was** a function of the laboratory dissolution conditions (temperature, time, stirring, **NaCl** concentration), so the concentrations of Ca^{++} and $SO_4^{=}$ and the wt **%** insoluble residue values have little significance by themselves and should be used with caution. The total anhydrite contents of these original samples were the sum of the Ca^{++} and $SO_4^{=}$ in the solutions plus the insoluble residues. The analyzed cores contained from 1.9 to 6.1 wt % anhydrite. Anhydrite content of the cores appeared to change with sample depth but not in a regular manner. The variation of anhydrite solubility with changing dissolution conditions will affect any attempt to calculate the volume of insoluble residue produced during the leaching of a cavern in **a salt** dome.

Densities of several core samples **were** determined and insoluble residue from one sample **was** counted for radioactivity. No radioactivity was detected in the sample.

CONTENTS

TABLES

FIGURES

INTRODUCTION

The goal of the Strategic Petroleum Reserve (SPR) program is to protect the United States from a temporary cutoff of imported crude oil by stockpiling a reserve of oil in caverns in Gulf Coast salt domes. Some suitable caverns already exist as a result of solution mining activities by commercial mining companies. Most of the caverns for the program, however, will. be solution mined specifically for the SPR program.

The tasks assigned to Sandia National laboratories include conducting a geotechnical program and providing interim technical support for the leaching of the first five caverns in the Bryan Mound, Texas, salt dome. This report describes chemical, mineralogical and petrological work done at Sandia as of May 1, 1980 in support of Bryan Mound activities. The results reported here will contribute to the Bryan Mound site characterization report and to the interpretation of the results of mechanical properties tests of Bryan Mound salt and will serve to verify and clarify the results of other tests made at Bryan Mound and on Bryan Mound geological material. This report also serves to document the procedures used in chemical analysis of SPR samples at Sandia.

EXPLANATIONS

Units

For consistency with work in the field, English units of length will be used in this report. All construction and engineering work for the SPR, most of the sample collecting equipment (such as core tubes), sample identification numbers and well depths employ traditional English units of measurement. Depths originally measured in feet will not be converted to meters; industry standard four inch core will not be referred to as 10.16 cm core. In cases where measurements were made in our laboratory, metric equivalents

will be given in addition to the English units. Weights and chemical

measurements made in our laboratory will be given in metric units to be

consistent with standard practice. For reference: 1 mile ≈ 1.61 kilometers,

1 foot ≈ 30.5 centimeters, 1 inch ≈ 25.4 millimeters.

Mineral Names

In many of the sections that follow, minerals are identified and dis-
cussed by their mineralogical names. Some later sections of this report
discuss chemical analysis data for dissolved samples. To provide a con-
nection between the mineralogical names and chemical analyses, Table 1
lists the minerals discussed in this report and their chemical formulas.
The chemical formulas will not be repeated each time a mineral name is used.

Definitions

A glossary of some chemical and mineralogical terms that may not be
well known outside their specialties is provided at the end of this report.

X-ray Diffraction

Many mineral identifications by x-ray powder diffraction are reported
in the work that follows. These identifications were made using either a
Norelco diffractometer equipped with a wide-range goniometer and scintil-
lation detector or with a standard 114.6 mm **Debye-Scherrer** powder camera,
For a few samples, major elements **were** identified by qualitative analysis
using x-ray fluorescence. Only elements with atomic numbers greater than
12 (Magnesium) can be detected efficiently by this method. The elemental
information was used to help interpret the x-ray diffraction results.

Table 1. Mineral Names and Chemical Formulas

Anhydrite	$CaSO_4$
Ankerite	$(Ca,Mg,Fe)CO_3$
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Gypsum	$CaSO_4 \cdot 2H_2O$
Halite	$NaCl$
Hematite	$\alpha\text{-}Fe_2O_3$
Maghemite	$\gamma\text{-}Fe_2O_3$
Magnesite	$(Mg,Fe)CO_3$
Magnetite	Fe_3O_4
Quartz	SiO_2
Sylvite	KCl
Wüstite	FeO

Table 2. Densities of Bryan Mound Salt Core Samples as Determined
By Air Comparison Pycnometer

Sample		Density (g/cc)
BM-109B-3244/3245	(SPR-4)	2.18 ± 0.05
BM-109B-3247	(SPR-5)	2.16 ± 0.05
BM-107C-2503	(SPR-21)	2.17 ± 0.05
BM-107C-2511	(SPR-22)	2.17 ± 0.05
BM-108B-3316	(SPR-23)	2.16 ± 0.05
BM-108B-3332	(SPR-24)	2.17 ± 0.05

THE BRYAN MOUND SITE

The Bryan Mound salt dome is located about 50 miles south of Houston, Texas, near the town of **Freeport** and is about 2 miles inland from the Gulf of Mexico. The salt dome itself has a roughly circular cross-section ranging from about 1 to 1.4 miles across. The top of the salt is about 1100 feet below sea level and is covered by **caprock** which varies in thickness from 350 feet over the center of the **dome** to near zero thickness at the edges. The **caprock** is composed primarily of limestone, **gypsum,** anhydrite and sulfur. The overburden above the **caprock** consists of marine sediments (shale, sands, clays). Since 1901 Bryan Mound salt dome has been the site of exploration and canmercial production of small amounts of oil and large amounts of sulfur and brine. The DOE obtained the Bryan Mound site for inclusion in the SPR in 1977. Details on the history and characterization of the Bryan Mound site may be found in **D'Appolonia** (1980).

SAMPLE TYPES AND NOMENCLATURE

A series of wells has already been drilled for the SPR at Bryan Mound. The wells will be enlarged by solution mining *to* form the caverns needed for oil storage. Completed caverns will be approximately 250 feet in diameter and 2000 feet high. Multiple wells have been drilled at each cavern site that is discussed in this report. During leaching the wells will expand and coalesce to form one cavern. Each cavern site is designated with a three-digit number and each well at that site is identified by a letter - A, B, or C. The three **wells** at cavern site 109 are thus designated as wells **109A, 109B** and **109C.**

Three distinct types of salt samples **were** received from the Bryan Mound sites. They were core samples, drill cuttings and sidewall samples. Core

samples **were** solid cylinders of rock (mostly salt) obtained during the drilling of the wells. Depths for core samples were well known. Drill cuttings **were** chips of rock brought to the surface by the circulating drilling mud and collected. Depths for these samples have some uncertainty because of uncertainties in their transit **time** to the surface. Sidewall samples were collected by a mechanical device which collected an approximately **7/8** inch diameter by one inch long plug of rock from the walls of the wells after they were drilled. The depth of collection for sidewall samples were weil known.

The samples analyzed in this study are listed in Appendix I together with a brief description of each sample as it **was** received. The sample numbers are descriptive of the locations from which the samples **were** collected. For example, sample **BM-109B-3247** came from Bryan Mound salt dome, well number **109B,** depth 3247 feet below the Kelly bushing. The depth is given to the nearest foot. A depth notation like 324413245 on a core sample means the sample came from the boundary between the 3244 and 3245 foot segments. A single drill cutting sample consists of cuttings produced from drilling several feet of well. The depths of these samples indicate a range, e.g., BM-1056-333413364.

A second shorter number was assigned to each sample as it was received in the chemistry laboratory. For example, sample **BM-109B-3247** was assigned the number SPR-5. This shorter number was easier to carry through laboratory reports and notebooks without transcription error and permitted the assignment of a unique number for each sample in cases where two samples were taken from the same one-foot core segment or from the same bag of drill cuttings.

Core samples were used for several purposes:

1. Identification of major minerals by x-ray diffraction.

2. Source material for petrographic thin sections. Sections were examined
    microscopically to determine texture of samples and the placement of
    minor minerals.

3. Determination of core density.

4. Starting material for dissolution experiments to determine nature
    of insoluble material in core.

5. Source material for determining water soluble portion of core.

Preparation and Examination of Thin Sections

Thin sections **were** made from three samples: **BM-109B-3244/3245 (SPR-4),**
dark vein material from **BM-107C-2511** (SPR-22) and white, vein free material
from the same sample. A "thick" section was made from **BM-109B-3247** (SPR-5).

To make a thin section, a piece of core about 2 x 4 cm (0.8 x 1.6 inch)
was selected and one side was ground flat on **SiC** abrasive paper. The final
grinding on the flat side was made with 600 grit abrasive paper. The piece
was then attached to a standard 1 x 3 inch glass microscope slide with epoxy,
flat side toward the slide. After the epoxy cured, the part of the sample
above the slide was ground flat and parallel to the slide. Grinding con-
tinued until the slab of sample above the slide **was** as thin as possible.
For these samples, the final salt section was 100 to 200 microns (0.004 to
0.008) inch thick. 600 grit **SiC** abrasive paper was used for the final grinding.
All grinding was done dry.

The sections produced were much thicker than a standard 30 micron (0.0012 inch)
thick rock thin section made on automatic thin section equipment using diamond

abrasive. Because the salt samples were made up of clear minerals with relatively large grain sizes, the "homemade" sections described here served their purpose very well in spite of their thickness. The "thick" section of SPR-5 was made in the same way except that grinding was stopped when the section was about 3 mm (0.12 inch) thick.

Figures la and lb show photomicrographs of the thin section of SPR-4. Magnifications are given on the figures. The roughly rectangular grains are anhydrite grains set in a halite matrix which makes up the rest of the view in each photo. The dark round spots are air bubbles in the epoxy. Irregular dark lines are halite grain boundaries. Note that the anhydrite grains are reasonably evenly distributed through the halite grains rather than concentrated at grain boundaries. This intimate mixture of halite and anhydrite is evidence that they are cogenetic. Examination of the SPR-5 thick section showed the same result. The thick section allowed observation in the depth dimension by changing the focal plane of the microscope. Some halite-halite grain boundaries in the thick section were covered with round to sausage-shaped features (Figure 2). These features do not have the negative crystal shape characteristic of fluid inclusions in salt. Further examination, even under high magnification, showed no gas-liquid interfaces in the features. One possible explanation of the features is that they are voids due to parting along the halite-halite interface produced when pressure was relieved in the core section. Before coring, this salt was under the lithostatic pressure of over 3000 feet of salt and rock. This pressure would have held the halite grains tightly together.

The thin sections of the dark vein and light colored part of SPR-22 are shown in Figures 3a and 3b. Anhydrite grains are very widely spaced in the light area. The dark veins are made up of concentrations of anhydrite grains.
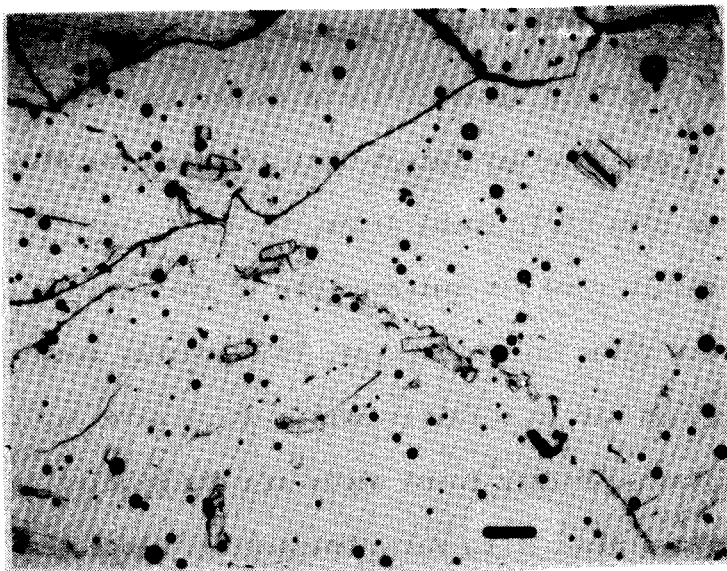
Figure la.   Photomicrograph of a thin section of **SPR-4 (BM-109B-3244/3245).**
Rectangular grainsareanhydrite in a halite matrix. Dark lines
are halite grain boundaries; dark round spots are bubbles in the
epoxy.   Scale bar is 300 microns.
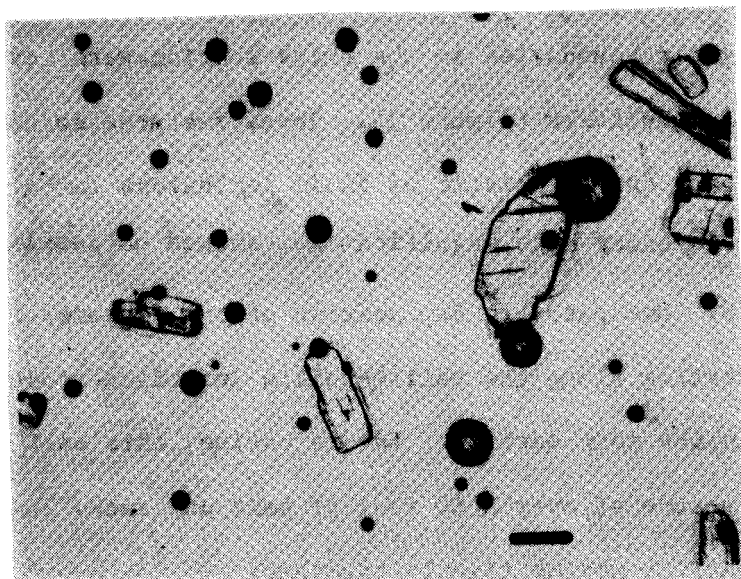
Figure **1b.**   Same as Fig. la except no halite grain boundaries are in the
frame and scale bar is 150 microns,

Figure 2. Photomicrograph of SPR-5 **(BM-109B-3247)** thick section. Possible void areas on halite-halite grain boundary are in the right center part of the photo. Scale bar 300 microns.
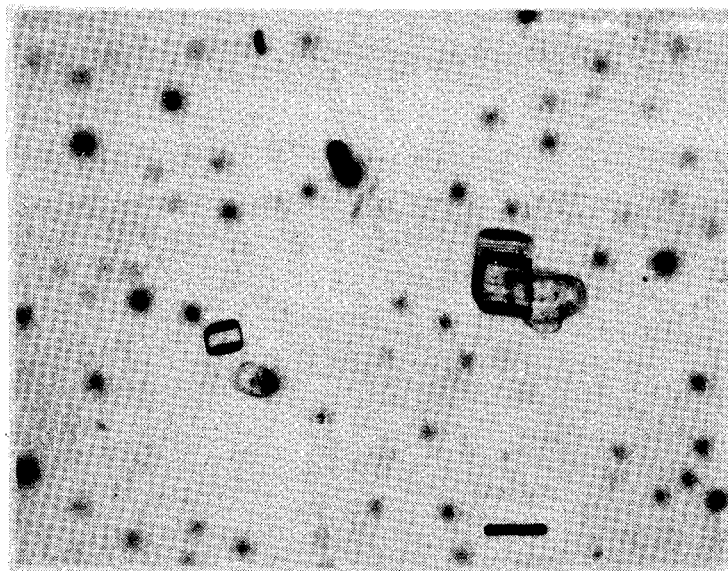
Figure 3a.   Photomicrograph of a thin section from *a* clear area of SPR-22
             (BM-107C-2511). A few anhydrite grains are present near the
             center of the frame. Fuzzy, dark, round spots are bubbles in the
             epoxy. Scale bar 150 microns.

Figure 3b.   Same as 3a except this section includes a dark vein which is
             made up of many closely packed anhydrite grains. Scale bar
             150 microns.

The smaller grain size of the anhydrite-rich area produced the darker coloration in these areas. The origin of the veins is open to speculation. Such veins could be **remnants** of anhydrite (or precursor gypsum) layers produced during the original formation of the evaporite deposit. They could also have been formed mechanically by exclusion from halite as the halite underwent plastic flow at some time during its history - perhaps during the **doming** of the salt.

Major Minerals by X-Ray Diffraction

Samples of salt cores **BM-109B-3244/3245, BM-109B-3247,** BM-109A-2346 and **BM-107A-3964** (SPR-4, 5, 6, 7 respectively) were characterized with the x-ray diffractometer to determine mineralogy. Halite was the major mineral in all four samples. Anhydrite was also detected in all four but was much less abundant than halite. Sylvite was probably present in SPR-6 and 7, but these lines were too weak for a positive identification.

Core sample **BM-107C-2511** (SPR-22) contained a dark vein as described in the sample description section. Mineralogy of a sample of the dark vein material and a sample of the white core material away from the vein were determined by x-ray diffraction. Only halite was identified in the white part of the core, while halite and minor anhydrite were detected in the dark vein material. This finding indicates that anhydrite is enriched in the vein material, as observed in the thin sections.

Densities

Densities of seven samples **were** determined with an air canparison **pycno-**meter. The samples **and** results are listed in Table 2. All are equal to that of halite within the experimental uncertainty. The density of halite is 2.16 g/cc; the density of anhydrite is 3.0 g/cc.

Dissolution of Cores and Treatment of the Insoluble Residues

Eight core samples were dissolved and the insoluble residue was obtained from each. These samples are listed in Table 3.

Each core sample was cleaned by sanding all cut surfaces on a belt sander or with abrasive paper to remove surface material that had been in contact with drilling mud. These sanded surfaces were further cleaned by wiping them with a damp paper towel. The freshly broken ends of six of the core samples were cleaned only by wiping away any visible foreign matter.

In some cases about 200 g of sample was used and the final solution diluted to 1000 mL. In other cases about 100 g of core was used and the final volume of the solution was 500 mL. After weighing each sample, it was placed in a large flask with about 2/3 of the final desired volume of deionized water. The flask was frequently agitated by hand until all or nearly all of the salt had dissolved. This normally took two to three working days with agitation about every hour. A magnetic stirrer was used instead of hand agitation in some cases. Dissolution by this method took one to one-and-a-.half working days.

After dissolution the liquid was filtered through a tared glass fiber filter paper into the appropriate sized volumetric flask with either 500 or 1000 mL capabity. The dissolution flask was rinsed several times with deionized water to dissolve any remaining salt and to transfer all undissolved matter to the filter paper. The residue in the filter paper was washed 10 or more times with small volumes of deionized water. All rinse and wash solutions were added to the volumetric flask. The volumetric flask was then filled to the mark, the density of the solution determined and the solution transferred to a plastic bottle. The brine solutions produced in this manner were analyzed chemically. The analyses of the brines will

Table 3.   Chemical Compositions of Bryan Mound Salt Core Samples. All values are in wt %.

			Soluble					
Sample	Na+	Ca^{++}	K+	Cl^-	$SO_4^=$	Insoluble*	Sum	Total $CaSO_4$[†]
SPR-4	35.3	0.360	0.046	57.2	0.854	4.4	98.2	5.6
SPR-5	35.9	0.420	0.050	57.2	1.00	4.2	98.8	5.6
SPR-6	37.0	0.300	0.007	57.9	0.64	3.13	99.0	4.1
SPR-7	37.3	0.495	0.061	58.4	1116	1.84	99.3	3.5
SPR-21	36.8	0.173	0.026	59.1	0.42	1.31	97.8	1.9
SPR-22	36.7	0.266	0.024	58.0	0.64	2.56	98.2	3.5
SPR-23	35.6	0.286	0.045	57.1	0.70	4.38	98.1	5.4
SPR-24	35.9	0.348	0.046	56.6	0.84	4.87	98.6	6.1

SPR-4 = BM-109B-3244/3245   SPR-5 = BM-109B-3247   SPR-6   = BM-109A-2346   SPR-7 = BM-107A-3964

SPR-21 = BM-107C-2503   SPR-22 = BM-107C-2511   SPR-23 = BM-108B-3316   SPR-24 = BM-108B-3332

*Insoluble residue left after dissolution.   Amount is dependent on dissolution conditions. X-ray
  diffraction shows material to be anhydrite $(CaSO_4)$.

†Sum of Insoluble + Ca^{++} + $SO_4^=$. See text for explanation.

be discussed in a later section of this report.

The glass fiber filters containing the insoluble residues were dried to a constant weight at **50°C,** and the weight of the residue was calculated by difference. **50°C was** selected as a drying temperature because it is well below temperature at which gypsum is known to begin losing its water of hydration.

An aliquot of insoluble residue from each sample was characterized by x-ray diffraction to determine mineralogy. In all cases only anhydrite was detected. Also', a small sample of residue from SPR-4 was taken before the 50°C drying step and characterized by x-ray diffraction. This material was also only anhydrite, indicating no mineral phases had been altered by the drying process.

Some of the residue grains were examined microscopically and photographed (Figure 4). The grains have the optical properties of euhedral anhydrite grains.

The wt **%** insolubles for the original cores are shown in Table **3.** Care should be exercised in using these figures because the amount of insoluble residue produced depended on the dissolution conditions used in the laboratory. The analyses of the brines produced during the dissolution of the cores indicate that a significant portion of the anhydrite dissolved. The amount of anhydrite residue produced during solution mining of a cavern will depend on many factors, among them the amount of fresh water used, contact time between the **water** and the anhydrite, **NaCl** concentration of the solution, and solution temperature as **well** as the anhydrite content of the original salt. See, **for** example, Figure 5 for anhydrite solubility as a function of **NaCl** content of solution and Figure 6 for a plot of anhydrite solubility as a function of temperature.
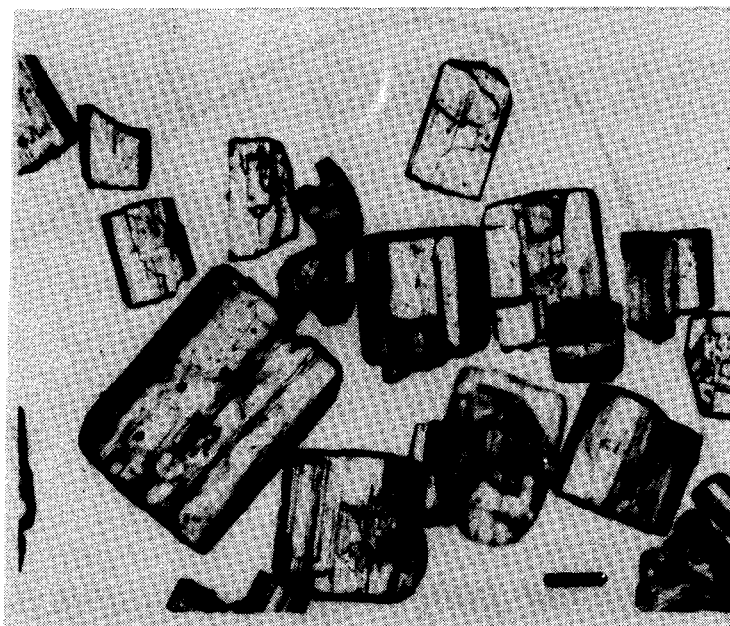
Figure 4. Photomicrograph of a group of anhydrfte crystals that made up part of the insoluble residue from SPR-4 (BM-109B-3244/3245). Scale bar is 150 microns,
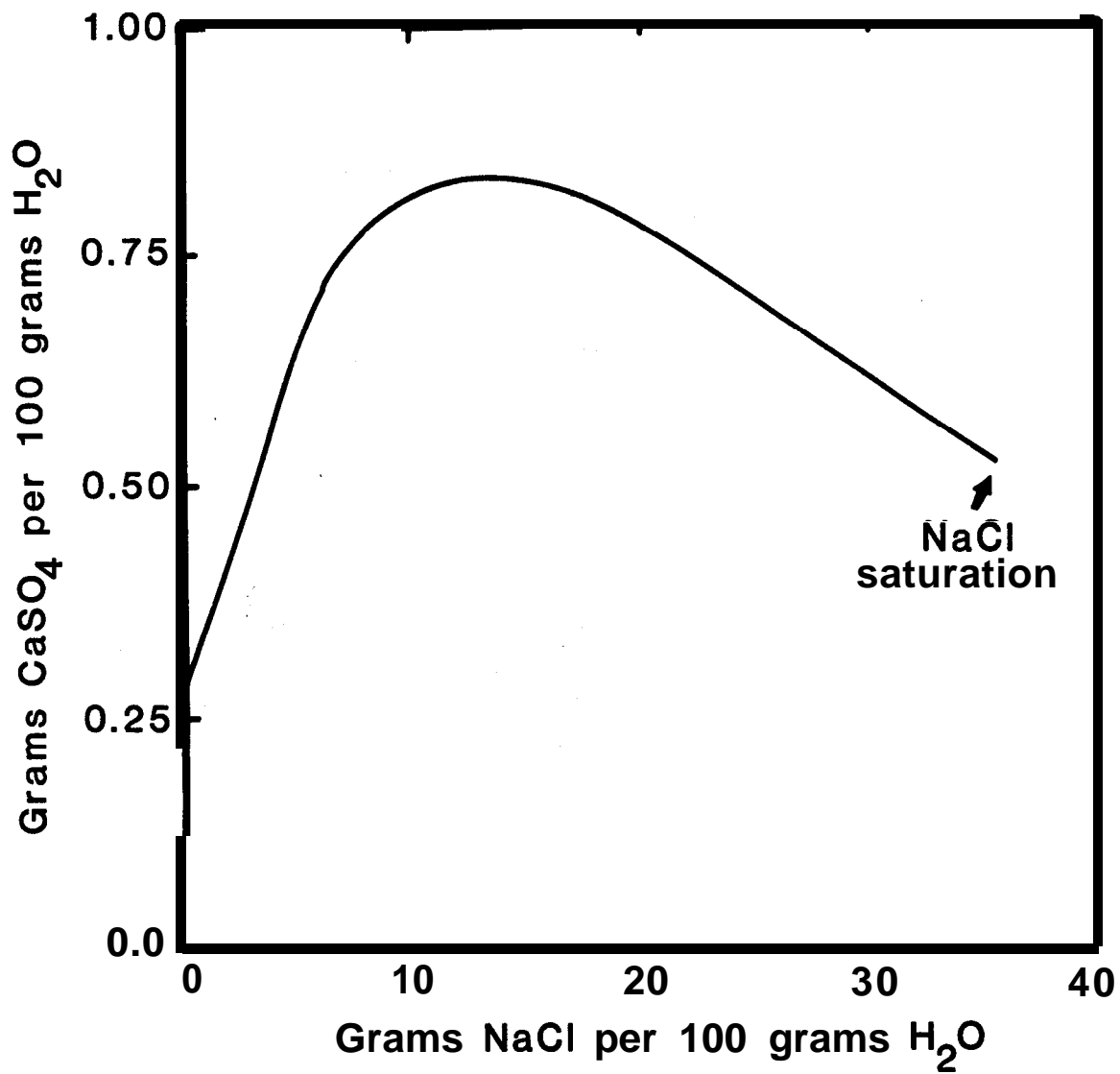
Figure 5.   Solubility of anhydrite as a function of **NaCl** content of
the solution at 25°C.   From data in **Madgin** and Swales (1956).
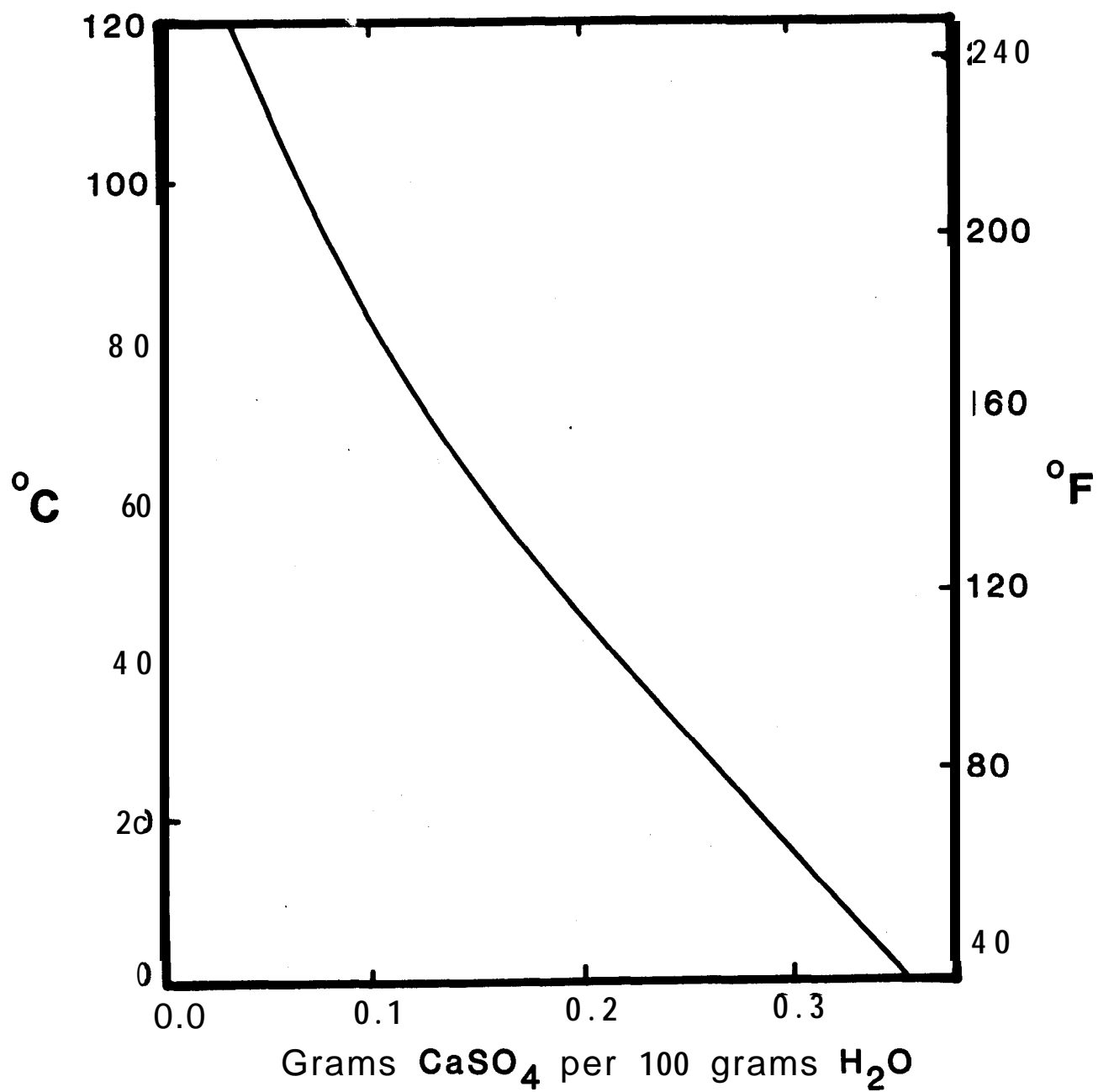
Figure 6.   Solubility of anhydrite in pure water as a
            function of temperature.

Search for Radioactivity in the Insoluble Residue

The insoluble residue from SPR-5 (BM-109B-3247) was counted on a Ge(Li) detector to search for any radioactivity present. None was detected above background. Activity seen in the background includes ^{214}Pb, ^{208}Tl, ^{214}Bi, ^{228}Ac, and ^{40}K. The first four are due to decay of natural uranium and thorium in the concrete walls and floor of the counting room, and the ^{40}K is part of the natural K in the building materials of the counting room. Upper detection limits for these activities in the residue sample, in Curies per gram of residue, are 2×10^{-5}, 3×10^{-4}, 5×10^{-5}, 7×10^{-5} and 5×10^{-5}, respectively. To reiterate, these values are upper detection limits; no radioactivity above background was actually detected coming from the SPR-5 residue.

Analysis of Brine Solutions Produced by Dissolving Salt Cores

The dissolution of salt cores to produce brine solutions was described in a previous section. The final solutions produced were about 2/3 saturated with NaCl.

The solutions were analyzed for the cations and anions that are usually important in brines: Na^+, K^+, Ca^{++}, Mg^{++}, Cl-, $SO_4^=$, HCO_3^-, and $CO_3^=$. The Na^+ and K^+ were analyzed by atomic absorption. Ca* and Mg^{++} were analyzed by either atomic absorption or EDTA titration. Cl^-, HCO_3^-, and $CO_3^=$ were determined volumetrically, and $SO_4^=$ was determined gravimetrically. Details of the chemical procedures used are given in Appendix II of this report.

Results of these analyses are given in Table 3. Magnesium, carbonate and bicarbonate analyses were done for all samples, but none was detected in any of them. Detection limits for all samples were Mg^{++} less

20

than 1 x 10^{-4} wt %, HCO_3^- less than 0.005 wt % and $CO_3^=$ less than 0.005 wt %. In addition to the results of chemical analyses, Table 3 also contains the weight fraction of undissolved anhydrite recovered during dissolution of each sample. The sum column is the sum of all cations, anions and insoluble anhydrite.

Table 4 shows the data of Table 3 recalculated on a molar basis. Note that the moles of Ca^{++} are essentially equal to the moles of $SO_4^=$ for all samples, This result is strong evidence that all of the Ca^{++} and $SO_4^=$ in the solution were dissolved anhydrite. The moles of Na^+ plus K^+ (K^+ is insignificant compared to Na^+) should equal the moles of Cl^- in the solutions. This is nearly the case, but Na^+ is slightly low, probably due to a small systematic error in the Na analysis by atomic absorption. Concentrated Na^+ solutions like these require dilution to about 75 µg/g before analysis and thus are difficult to analyze without a systematic dilution error. If the concentrations of Na^+ were 2 to 4% (relative) higher than the values shown, agreement between the molar amounts of Na^+ and Cl^- would be improved and the sums in Table 3 would increase to nearly 100%.

Several other elemental analyses were carried out in just a few of the brines. These were done for reconnaissance purposes only. Results are listed in Table 5.

Discussion of Chemical Analysis Data

As stated above, the chemical data are consistent with the hypothesis that all Na^+ and Cl^- are from dissolved halite. The amount of K found is very minor compared with Na. The K was probably also in the core in the form of chloride , possibly as a very few, very small grains of sylvite or

Table 4. Chemical Composition of Bryan Mound Salt Core Samples in Molar Units.
All values are moles per 100 g of core,

Sample	Na+	Ca^{++}	K^+	Cl^-	$SO_4^=$
SPR-4	1.54	0.00898	0.0012	1.61	0.00889
SPR-5	1.56	0.0105	0.0013	1.61	0.0104
SPR-6	1.61	0.00749	0.00018	1.63	0.0067
SPR-7	1.62	0.0124	0.0016	1.65	0.0121
SPR-2i	1.60	0.00432	0.00066	1.67	0.0044
SPR-22	1.60	0.00664	0.00061	1.64	0.0067
SPR-23	1.55	0.00714	0.00115	1.61	0.0073
SPR-24	1.56	0.00868	0.0012	1.60	0.0087

Table 5. Other Cations and Anions Analyzed in Selected Core Samples.
All values are in wt %.

Sample	Br^-	Li^+	Sr^{++}
SPR-5	$\leq$0.005*	----	----
SPR-6	----	$\leq$0.001	$\leq$0.001
SPR-7		~0.001	LO.001
SPR-21	0.008+0.0002	----	----
SPR-23	~0.005"	----	----

Br^- by ion chromatograph; Li^+ and Sr^{++} by atomic absorption.

*Br^- was observed above background in this sample but at too
low a level to permit calculation of an accurate concentration.

as K substituted for Na in the halite lattice. Deer, et al., (1962) state that there is little replacement of Na by K in halite. However, the levels reported here are about two orders of magnitude lower than values reported in Deer et al. (1962) for K in halite samples. Thus the detection of K in these cores does not necessarily imply the presence of sylvite.

All Ca^{++} and $SO_4^=$ in the solution appear to be due to the dissolution of anhydrite. Madgin and Swales (1956) and Braitsch (1971) give curves of solubililty of anhydrite as a function of NaCl content of the solution. Figure 5 is a plot of the data from Madgin and Swales (1956) for 25°C. Anhydrite solubility is at a minimum of about 0.26 g $CaSO_4$/100 g H_2O when the solution contains no NaCl. Maximum solubility is about 0.84 g $CaSO_4$/100 g H_2O at about 14 g NaCl/100 g H_2O and drops to about 0.53 g $CaSO_4$/100 g H_2O at about NaCl saturation. It is estimated that during core dissolution in the laboratory, the solutions were nearly saturated with $CaSO_4$ before rinse water was added to the dissolution flask. There-fore, anhydrite dissolution was fairly rapid under the conditions used in this work, but the fraction of anhydrite that will be dissolved during solution mining of a cavern may be strongly dependent on dissolution conditions.

Another uncertainty in predicting the behavior of anhydrite during dissolution arises from the temperature dependence of anhydrite solu-bility. Braitsch (1971) presents a curve showing that the solubililty of anhydrite in pure water decreases with increasing temperature (Figure 6).

There does appear to be a variation of $CaSO_4$ content with depth. Figure 7 shows a plot of total $CaSO_4$ content of the eight analyzed core samples as a function of the depth from which the samples were collected. Samples from each well are indicated by a different symbol; total CaSO4
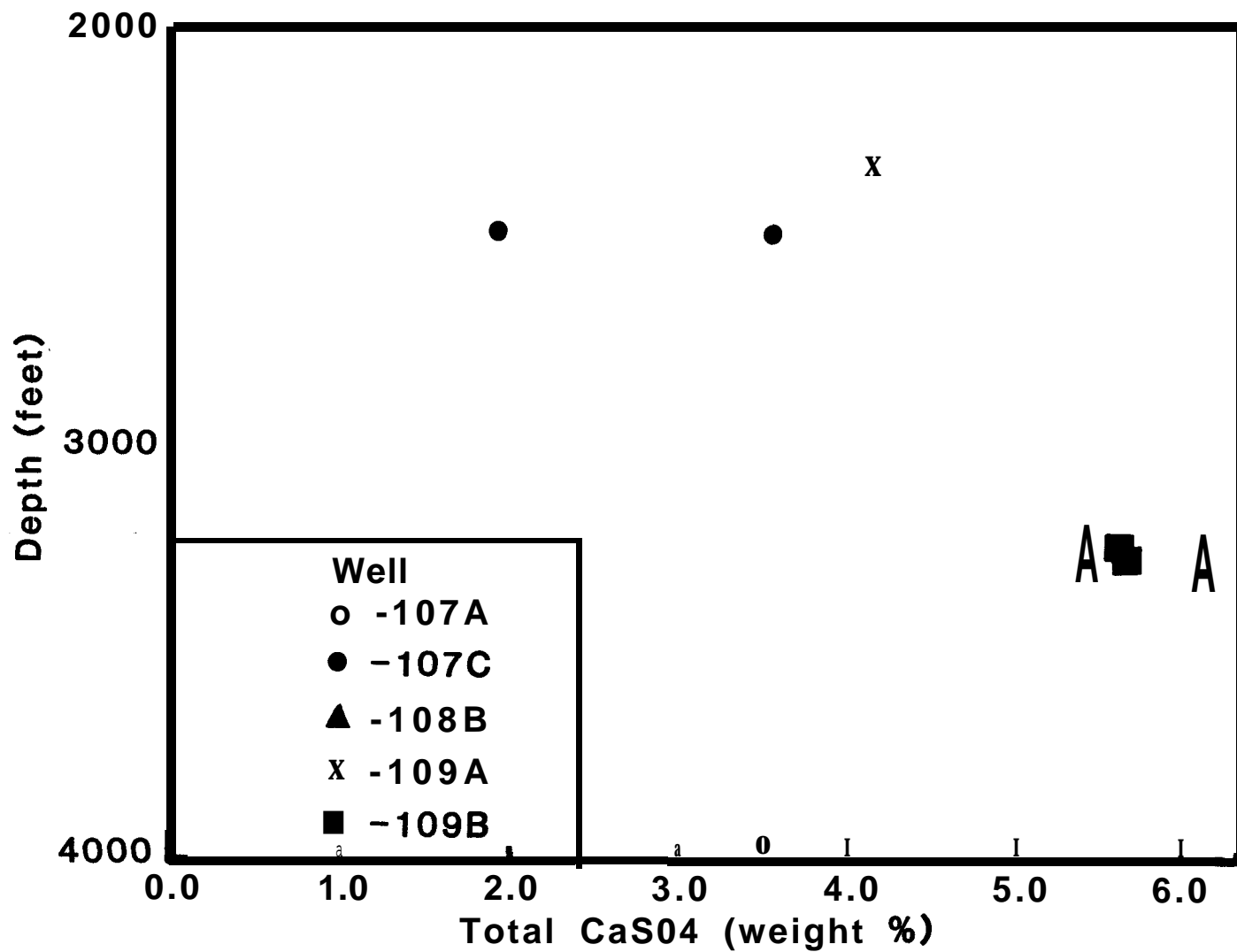
Figure 7.   Total CaSO$_4$ content vs. depth for eight Bryan
Mound Core Samples.   From Braitsch (1971).

values are taken from Table 3. The eight samples fall in three different depth ranges centered at about 2300 feet, 3300 feet and 4000 feet. The shallow group has $CaSO_4$ contents ranging from about 1.5 to 4.1 wt %, the middle group from about 5 to 6 wt % and the deep sample about 3.5 wt %. The total $CaSO_4$ content of the core samples appear to be dependent on depth, but the relationship is not regular.

Some Conclusions from Analysis of Core Samples

The salt core samples examined were all relatively pure halite (94 to 98 wt %). Anhydrite was the only significant impurity, ranging from about 2 to 6 wt % for the eight samples analyzed. No sylvite was found in any of these cores. Based on K^+ content of the cores, the maximum sylvite contents possible in the samples ranged from 0.01 to 0.12 wt %.

The anhydrite occurred as distinct euhedral grains with grain sizes from tens to hundreds of microns (about 0.004 to 0.020 inch). Anhydrite crystals were spread uniformly through halite grains, not concentrated at grain boundaries. Dark veins in some samples were regions concentrated in anhydrite crystals. The location and relative abundance of anhydrite grains could affect mechanical properties of the salt, particularly flow and strength.

The amount of the anhydrite that went into solution when the halite in the salt cores was dissolved is a strong function of the laboratory dissolution conditions. This means attempts to calculate the quantity of insoluble residue produced during leaching of a cavern at Bryan Mound will have many uncertainties. The best estimate of the amount of anhydrite in the core samples is the Total $CaSO_4$ column of Table 3. These values could be used to estimate an upper limit for the insoluble residue produced during cavern formation. Total anhydrite content of the core samples does

vary with the location from which the core was collected (depth, well), but the variation is not regular.

Other features observed in this work which should be considered in evaluating mechanical properties of the cores are variability in halite grain size from core to core and the presence of a foliated texture in some samples.

No radioactivity was detected above background in the residue sample checked for radioactivity.

MINERALOGY OF SIDEWALL SAMPLES BY X-RAY DIFFRACTION

Prof. William P. Moran of the University of Tulsa received the sidewall samples from the Bryan Mound wells and determined their mineralogy by x-ray diffraction (Moran, 1979). Geophysical logs of the same wells indicated layers of shale or anhydrite might be present in some areas. Evidence for such layers was not mentioned in the University of Tulsa reports on the sidewall samples. The samples from the areas in question were brought to Sandia for re-examination.

A diffractometer was used to obtain the x-ray data on the sidewall samples. The material run was picked from the sample jar and selected to contain part of each mineral phase visible to the naked eye. As a result of this selection scheme, the samples did not necessarily have the same relative abundances of each mineral as did the original bulk sample. Instead, the selection scheme was intended to enhance the chance of detecting minor phases in the sample. Table 6 lists the sidewall samples run at Sandia, the minerals that were identi-fied, and the minerals that were identified in the same samples at the University of Tulsa.

Halite was the daninant mineral in all samples examined at Sandia. Sylvite was easily detected in BM-108A-2397 (SPR-17) and was consistent with the pink color of the sample. Sylvite is typically pink or red in color.

Table 6. Minerals Identified in Sidewall Samples by X-Ray Diffraction.
X-ray diffraction normally will not detect minerals making up
less than about 5 wt % of the sample.

<u>Minerals Identified</u>

Sample	Sandia	U. of Tulsa*
BM-108A-2397 (SPR-17)	Halite Sylvite	**Halilte** Sylvite
BM-108A-2682 (SPR-18)	Halite Anhydrite Quartz	Halite Anhydrite Quartz Sylvite
BM-108A-3544 (SPR-19)	Halite	Halite Sylvite
BM-108A-3546 (SPR-20)	Halite Anhydrite Possible sylvite	Halite Anhydrite Sylvite
BM-102C-2532 (SPR-25)	Halite Anhydrite	Halite Sylvite
BM-102C-2566 (SPR-26)	Halite Anhydrite	Halite Anhydrite Sylvite

*Moran (1979)

Sylvite is listed in Table 6 as "possible" in **BM-108A-3546** (SPR-20). The strongest sylvite line was observed as a small peak in the trace. Other sylvite peaks **were** too weak to be seen above the background, so the presence of sylvite in the sample could not be confirmed.

The report from the University of Tulsa lists sylvite in the four remaining samples also. Two possible reasons for the absence of detectable sylvite in the results of the Sandia study are: 1. The sylvite in the original sample could have consisted of only a few sylvite grains which were consumed during the University of Tulsa study. 2. The diffractometer scans made at Sandia did not include long integrations at the locations of sylvite peaks. If the University of Tulsa study included such long integration times, sensistivity for the detection of sylvite would be increased.

The other discrepancy between the two sets of data in Table 6 is the presence of anhydrite in the Sandia aliquot of sample **BM-102C-2532** (SPR-25) but not in the University of Tulsa aliquot. The reason for this disagreement is not known; sample inhomogeneity is a possibility.

Conclusions From the Analysis of Sidewall Samples

1. The University of Tulsa work accurately describes the mineralogy of the samples and can be used to assist in interpreting well logs.
2. There is no clear evidence from the sidewall samples to support reports of shale, clay or anhydrite layers in any'of the areas sampled by the sidewall samples.

EXAMINATION OF DRILL CUTTINGS

Wells BM-105B and **105C**

The four drill cuttings samples from wells 105B and **105C** were examined under a stereomicroscope. Several types of grains, distinguished mostly

by color, were seen in each sample. Aliquots of each of these grain types

were picked out of the sample using tweezers. The aliquots were labeled

by sample name and color. They were then ground in an agate mortar, packed

into 0.3 mm diameter glass capillary tubes and analyzed by x-ray diffraction

to determine mineralogy. The aliquots picked from each sample are described

below. Only some of the identified minerals are given in these descriptions.

A complete list of all identified minerals in each aliquot is given in Table 7.

BM-105B-1585/1615 (SPR-8)

Light - Frosty and clear white grains. A couple of grains had a pink color
       indicating the possible presence of a small amount of sylvite although
       sylvite was not detected by x-ray diffraction.

Gray - This aliquot was made up of clumps of a dirty looking fine-grained
       material. Qualitative elemental analysis of this aliquot by x-ray
       fluorescence identified Ca, Fe, Cl, Si as the main elements in the
       sample. **Lesser** amounts of S, Mn, and K were also present. (Only
       elements with an atomic number greater than Mg are detected effici-
       ently by this method.) Calcite was the major mineral observed by x-ray
       diffraction. Many lines in the pattern, including some strong lines,
       corresponded well with the pattern for elemental sulfur (or some **iso-**
       structural compound). Elemental sulfur could be present as a decomposi-
       tion product of sulfate derived from anhydrite **($CaSO_4$)** or as contamination
       by S rich **caprock.**

Green - A couple of fragments with a green color like that of oxidized copper
       were found. Qualitative analysis by x-ray fluorescence found Fe, Ca,
       Cl, Si, Ti, K and S as the major elements heavier than Mg. Copper was
       not detected. Quartz was the major mineral identified. Many other weak
       x-ray lines were present in the x-ray diffraction pattern and could be

Table 7. Minerals Identified in Drill Cuttings Samples

BM-105B-1585/1615 (SPR-8)

      Light - Halite (major); anhydrite and quartz (minor).

      Gray - Calcite (major); quartz (minor); possible halite and sulfur.

      Green - Quartz (major); many other weak lines - possible anhydrite,

              halite, sylvite, calcite or other minerals.

      Dark - Halite and magnetite (major); anhydrite and quartz (minor);

              possible wustite, hematite, other iron oxides.

BM-105B-1615/1645 (SPR-9)

      Light - Halite (major); anhydrite (trace); possible sylvite.

      Dark - Halite and dolomite (major); possible sylvite and anhydrite.

BM-105C-3334/3364 (SPR-10)

      Light - **Halite** (major); anhydrite (minor); possible quartz.

      Dark - Halite and anhydrite (major); quartz (minor).

BM-105C-3426/3457 (SPR-11)

      Light - Halite (major); anhydrite (minor).

      Dark - Halite and anhydrite (major); quartz (minor).

BM-110A-3632/3663 (SPR-12)

      Halite and anhydrite.

BM-110A-3663/3694 (SPR-13)

      Light - Halite and anhydrite.

      Dark - Ankerite, magnesite, halite, possible quartz.

BM-110C-3670/3680 (SPR-14)

      Halite and anhydrite.

BM-110C-3700/3710 (SPR-15)

      Light - **Halite** and anhydrite.

      Dark - Ankerite, magnesite, halite, possible quartz.

BM-110C-3790/3800 (SPR-16)

      Light - Halite and anhydrite.

      Dark - Maghemite and/or magnetite, halite.

accounted for by a mixture of anhydrite, sylvite, halite and calcite, although no positive identification could be made.

Dark — Grains **were** nearly all black. Some looked like rust flakes and most were attracted by a hand magnet. Magnetite was one major mineral found in the aliquot.

BM-105B-1615/1645(SPR-9)

Light — Almost entirely clear and frosty white grains.

Dark — This sample consisted of one large dark lump that looked like dirty fine-grained salt. Qualitative elemental analysis by x-ray fluorescence found Ca, Cl, Fe, K, Si, and S in the sample. Halite and dolomite were the major minerals identified.

BM-105C-3334/3364(SPR-10)

Light — Mostly frosty white rounded fragments with dirty surfaces. A few grains were clear white.

Dark — Lumps of fine-grained dirty (black) salt which were very common in this bag of drill cuttings. A few grains looked like rust flakes and were attracted to a hand magnet. The more plentiful rounded black lumps were not magnetic.

BM-105C-3426/3457(SPR-11)

Light — Rounded clear and frosty white grains. A few grains appear to have striated surfaces. Many of the grains contained small black inclusions.

Dark — Lumps of fine-grained dirty salt. Pure dark grains were very rare. Most of the dark material was very fine grains on the surface of or included inside of white grains.

Halite with minor *amounts of anhydrite made up the great majority of all four of these drill cuttings samples. Among the minor phases picked out of the samples, the outstanding features **were** the presence of carbonate minerals (calcite

and dolomite), and the presence of iron oxides. These minerals were not observed in the Bryan Mound core samples or sidewall samples. The **caprock** of the Bryan Mound salt dome, known to contain carbonate minerals, could be the source of the carbonates in the drill cuttings. The carbonates could also be secondary reaction products due to reaction of the rock with drilling mud and the drill stem. The composition of the drilling mud is unknown, but it is known to be very basic (**pH** 12 to 13) and to be saturated with **NaCl**. Since drill cuttings were carried to the surface by the drilling mud, there was ample opportunity for chemical reaction between elements in the rock, (such as Ca from anhydrite) and CO_3^- in the basic drilling mud (either from dissolved CO_2 or picked up from the **caprock**) to form calcite $(CaCO_3)$. The Mg needed to form dolomite could also be a canponent of the drilling mud. The brine in the mud probably corroded the iron in the drill bit or drill stem to form the various iron oxides found. The quartz found in several of the samples was also probably a canponent of the mud.

No clay or shale lumps were found in any of the four samples. If the drill bit had cut layers of either of these materials, no trace of it remained in the samples examined. It is not certain, though, that clay or shale would survive as recognizable particles after cutting and contact with the basic drilling mud.

Wells **BM-110A** and **110C**

Five additional samples of drill cuttings from wells **110A** and **110C** were examined for mineralogy by methods like those described above for the samples from wells 105B and **C.** Sample selection was based on well log data. One interpretation of logs for well **110A** placed shale at depth 3640 to 3715 feet and anhydrite at depth-3740 to 3750 feet. The corresponding layers in **110C** were placed at 3610 to 3665 feet and 3730 to 3740 feet, respectively. Another interpretation of the well logs called these zones "anomalous" without

identifying mineral or rock type (Beasley, 1980). Drill cuttings were avail-
able in 30 to 40 foot increments from well 110A and at about 10 foot increments
from well 110C. All samples from several hundred feet around each of the above
zones were examined visually. None of the samples contained anything that
looked like shale or rocks with major anhydrite. The five samples selected
for mineralogical analysis were the samples closest to the zones in question.
The visual characteristics of each of these samples **were** described in Appendix I
of this report and had no significant differences from the visual character-
istics of other'drill cuttings samples.

   Samples for x-ray diffraction were selected under a stereomicroscope
and prepared as described in the previous section. They are described below.
A complete tabulation of the minerals that were identified in each sample is
given in Table 7.

BM-110A-3652/3663 (SPR-12)

   All grains clear to frosty white. A few black rust-like flakes were present.
Water in the sample had a muddy color. One sample that contained as many black
flakes as possible was selected.

BM-110A-3663/3694 (SPR-13)

   Sample looked just like SPR-12 above. Iwo aliquots were taken.

Light - White grains and white grains with a few black inclusions.

Dark - Black grains only. The carbonates ankerite and magnesite were identified
      in this sample.

BM-110C-3670/3680 (SPR-14)

   Black grains were very rare in this sample. Only the white grains were
included in the x-ray diffraction sample.

BM-110C-3700/3710 (SPR-15)

   Sample looked just like SPR-14. Concentrates of both black and white grains

were made for x-ray diffraction. Ankerite and magnesite were identified in the dark material.

BM-110C-3790/3800 (SPR-16)

Sample was mostly white but contained many black rust-like flakes. Concentrates of both black and white materials were made for mineral identification. Iron oxides maghemite and/or magnetite were identified in the dark material. These two minerals are isostructural and thus could not be positively distinguished from each other using the x-ray powder pattern obtained.

As with the drill cuttings from wells 105B and C, halite with minor anhydrite made up the great majority of the material in the BM-110A and 110C drill cuttings. Among the rarer phases identified were carbonates of Ca, Fe and Mg, as well as iron oxides. The carbonates were probably either the result of contamination from the caprock or were formed by reaction of Ca from anhydrite with Fe, Mg and $CO_3^=$ in the drilling mud. The iron oxides may be corrosion products from the iron drill stem or bit in contact with brine. No sign of shale or major anhydrite was found, perhaps for reasons similar to those given in the discussion of well 105B and C samples.

Conclusions from Examination of Drill Cuttings

Examination of the drill cuttings has led to verification of the major mineralogy of the salt dome: Halite with minor anhydrite. The results have not revealed interbedded shale or anhydrite as indicated by some interpretations of well logs. It is not clear whether this disagreement is due to inadequate analyses of the drill cuttings or to misinterpretation of the logs.

The cuttings as received at the surface of the well were altered from their original condition. New phases were formed, possibly by reaction of the cuttings with basic mud and possibly by corrosion of the drill bit or stem. The samples

might also be contaminated with pieces of **caprock** or with minor phases added directly from the drilling mud. Quartz may have been introduced to the samples in this manner. Mechanical erosion during the trip from the formation depth to the surface and reaction with drilling mud could have altered or completely disaggregated some friable phases, shale or clay for for example, to the point they were no longer identifiable in the surface sample. Drill cuttings are the least desirable of the types of samples examined in this report.

ACKNOWLEDGMENTS

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GLOSSARY

Below are definitions of some chemical and geological terms used in this report. They may not be well known to readers whose specialities are outside of these fields.

aliquo t – A fraction of a complete sample or solution taken for analysis.

air comparison pycnometer – a device for measuring the density of a material based on the amount of air displaced by a known weight of the material.

diffractometer – see x-ray diffraction below.

disaggregated – came apart into individual particles. A rock may disaggregate into its individual mineral grains.

euhedral – a grain of a mineral bounded by its regular crystal faces.

friable – easily crumbled.

foliated – parallel lineation in a rock caused by segregation of minerals into parallel bands or by parallel elongation of many mineral grains.

isostructural – two or more chemical compounds with similar crystal structures.

Kelly bushing – the location on a drilling rig where the Kelly passes through the rotary table. Sometimes used as a reference point for measuring depths'in a drill hole. The Kelly bushing can be several tens of feet above the land surface, depending on the type of drilling rig.

phase – a homogeneous, physically distinct portion of matter in a nonhomogeneous system., e.g., each mineral in a rock is a phase.

stereomicroscope – a low power microscope with separate optics for each eye, designed to provide stereoscopic visual perception.

x-ray diffraction – a method of identifying minerals present in a sample by examining the angles at which x-rays are diffracted by the powdered sample. Diffraction patterns are recorded on film in a camera or on chart paper by an automatic diffractometer.

x-ray fluorescence - a method of identifying elements in a sample by identifying the characteristic x-rays emitted by the sample when it is excited by a source of monochromatic x-rays. Elements with atomic numbers greater than 12 (Mg) are identifiable by this method.

APPENDIX I

Descriptions of Samples Analyzed for This Report

BM-109B-3244/3245 (SPR-4) A slice of 4 inch diameter core ranging from about
1 to **1-3/8** inches (2.5 to 3.5 cm) thick. The sample was cut from just below
the mark on the core separating the 3244 and 3245 foot segments. Grain size –
approx. 0.1 to 0.2 inch (2 to 5 mm). Color – grayish white. Weight 621.9 g.

BM-109B-3247 (SPR-5) A slice of 4 inch diameter core about **1-1/4** inches thick.
The sample'was cut from the upper part of the 3247 foot segment. Grain size –
approx. 0.1 to 0.2 inch (2 to 5 mm). Color – grayish white. Weight – 681.1 g.

BM-109A-3246 (SPR-6) A piece of 4 inch diameter core ranging from **5/16** to **1-1/8**
inches (0.8 to 2.9 cm) thick. One end surface was a smooth saw cut and the
other an irregular broken surface. This piece was an end piece left after a
segment of core was cut for mechanical testing. Grain size – approx. 0.2 to
0.4 inch (5 to 10 mm). Color – grayish white. Weight – 308.4 g.

BM-107A-3964 (SPR-7) A piece of 4 inch diameter core ranging from **5/8** to **1-1/2**
inch (1.6 to 3.8 cm) thick. One end surface was a smooth saw cut and the

other an irregular broken surface. This piece was an end piece left after
a segment of core was cut for mechanical testing. Grain size – typically
0.4 to 0.6 inch (10 to 15 mm). Some grains were elongated to about 0.8
inch or more by less than 0.4 inch (20 by 10 mm). Elongated grains had their
long axes parallel giving the section a foliated texture. Color – grayish
white. Weight – 455.2 **g.**

BM-105B-1585/1615 (SPR-8) Wet drill cuttings in a plastic bag. Sample con-
sisted largely of whitish grains about 0.1 inch (3 mm) across* Some
black flakes about 0.04 to 0.1 inch (1 to 3 mm) across were present. Some
of the black flakes were attracted to a hand magnet.

BM-105B-1615/1645 (SPR-9) Wet drill cuttings in a plastic bag. Sample consisted largely of **whitish grains** 0.2 inch (5mm) and less across* A few black flakes 0.04 to 0.1 inch (1 to 3 mm) across were present. Some of the black flakes were attracted by a hand magnet.

BM-105C-3334/3364 (SPR-10) Wet drill cuttings in a plastic bag. Sample had a dark overall color. The majority of the sample consisted of clear or white grains less than 0.2 inch **(5mm)** across covered by a fine black silt-like material suspended in the water. Dark grains and lumps in the sample were not magnetic. A few black, flat flakes in the sample were attracted to a hand magnet.

BM-105C-3426/3457 (SPR-11) Wet drill cuttings in a plastic bag. The sample had a dark overall color but was less dark than SPR-10 above. The sample consisted of clear and white grains less than **0.1** inch (3mm) across covered with a black silt-like material suspended in the water.

BM-110A-3632/3663 (SPR-12) Wet drill cuttings in a plastic bag. Sample consisted primarily of whitish grains less than 0.1 inch **(3mm)** across. The aqueous liquid in the bag had a reddish-brown mud-like color. A few black flakes which were attracted to a hand magnet were present.

BM-110A-3663/3694 (SPR-13) Wet drill cuttings in a plastic bag. The sample consisted of white grains less than 0.16 inch (4mm) across. The liquid in the bag had a grayish cast. A few black grains were present, some were attracted to a hand magnet, and some were not.

BM-110C-3670/3680 (SPR-14) Wet drill cuttings in a plastic bag. The sample consisted of white grains less than 0.08 inch (2 mm) across. The grain size of-this sample was distinctly smaller than the previous two samples (SPR 12 and 13). The liquid in the sample was slightly brownish. A few black flakes were present.

BM-110C-3700/3710 (SPR-15) Sample description identical to SPR-14 above.

BM-110C-3790/3800 (SPR-16) Wet drill cuttings in a plastic bag. The
sample consisted of white -grains less than 0.1 inch (3 mm) across.
The liquid in the bag had a reddish-brown mud-like color. A few black
flakes were present. A large 0.4 x 0.8 inch (10 x 20 mm) piece of
bright red plastic or paint **was** also in the sample.

BM-108A-2397 (SPR-17) Sidewall sample in glass jar. Sample consists of white
and pink grains. Total volume of sample about 0.3 to **0.4** inch^3 (5 to 7 cc).

BM-108A-2682 SPR-18) Sidewall sample in glass jar. Sample was grayish-white.
Total volume of sample about 0.3 inch^3 **(5cc).**

BM-108A-3544 (SPR-19)' Sidewall sample in glass jar. Most of the material
was white. Some of the pieces had a tan colored crust. Total sample
'volume about 0.3 to 0.4 inch^3 (5 to 7 **cc).**

BM-108A-3546 (SPR-20) Sidewall sample in a glass jar. There were several
large lumps 0.4 to 1.2 inch (1 to 3 cm) in longest dimension and some
powder. Some of the lumps had a dark colored rind. Interiors of the
lumps were white. Total volume of the sample was about 0.3 to 0.4 inch^3
(5 to 7 cc).

BM-107C-2503 (SPR-21) A piece of 4 inch diameter core ranging from 0 to **1-3/8**
inch (0 to 3.5 cm) thick. One end surface was a smooth saw cut and the
other was an irregular broken surface. This piece was an end piece left
after a segment of core was cut for mechanical testing. A large euhedral
halite grain in the center of the core was about 1.2 inches (30 mm) across
and showed prominant cubic cleavage. Other grains in the core ranged down
to 0.04 to 0.08 inch (1 to 2 mm) across* Dark bands formed a zone about
3/4 inch (1.9 cm) **wide** near one edge of the section. The plane of the
dark bands was approximately parallel to the axis of the core. Except
for the dark bands, the sample was white in color. Weight **-** 344.3 **g.**

BM-107C-2511 (SPR-22) A piece of 4 inch diameter core ranging from **7/16** to **9/16** inch (1.1 to 1.4 cm) thick. One end surface was a smooth saw cut and the other was an irregular broken surface. This piece was an end piece left after a segment of core was cut for mechanical testing. A dark vein about **1-5/8** inches (4.1 cm) wide ran through the center of the sample. The dark vein was made up of several thinner dark bands. The plane of the dark bands was approximately parallel to the axis of the core. Except for the dark band, the sample was white in color. Grain size ranged from about 0.4 to 0.8 inch (1 to 20 mm) across. Weight **-** 231.6 **g.**

BM-108B-3316 **(SPR-23)** A piece of 4 inch diameter core ranging from 0 to **7/8** inch (0 to 2.2 cm) thick. One end surface was a smooth saw cut and the other was an irregular broken surface. This piece was an end piece after a segment of core was cut for mechanical testing. Color **-** white. Weight **-** 262.8 **g.**

BM-108B-3332 (SPR-24) A piece of 4 inch core ranging from 0 to **1-3/8** inches (0 to 3.5 cm) thick. One end was a smooth saw cut and the other an irregular broken surface. This piece was an end piece left after a segment of core was cut for mechanical testing. Grain size was 0.1 to 0.6 inch (3 to 15 mm) across. Color **-** white. Weight **-** 297.3 **g.**

BM-102C-2532 (SPR-25) Sidewall sample in a glass jar. Sample consisted of mainly white material with a dirty crust on some of the larger fragments. The largest pieces of the sample were about 0.4 inch (1 cm) across.

BM-102C-2566 (SPR-26) Sidewall sample in a glass jar. Sample consisted of one large lump about 1.2 inches (3 cm) across plus some smaller fragments and dust. The large lump had a dirty looking crust on its surface. The interior of the large lump was white to gray in color.

APPENDIX II

Chemical Analysis Procedures Used to Obtain the

Chemical Data Presented in This Report

Alkalinity of SPR Solutions

Scope : This method provides for the determination of the hydroxyl, carbonate or bicarbonate present in various mineral waters or for the determination of, carbonate and either hydroxide or bicarbonate in the waters.

Outline : The water sample is titrated with standard HCl first to the phenolphthalein endpoint. The titration is then continued to the methyl red endpoint. The titration to the phenolphthalein endpoint neutralizes all hydroxyl and converts carbonate to bicarbonate. The titration from the phenolphthalein endpoint to the methyl red endpoint converts bicarbonate to H_2CO_3 which decomposes to CO_2 plus water.

Reference: J. S. Fritz and G. H. Schenk, Jr., Quantitative Analytical Chemistry. Boston, MA Allyn Bacon, Inc., 1966.

Apparatus : Usual laboratory glassware. Volumetric glassware – Class A or equivalent.

Reagents : All reagents are "analytical reagent" grade.

Hydrochloric acid, 0.01 N. and 0.1 N. – Both standardized against Tris(hydroxymethyl)aminomethane.

Phenolphthalein indicator solution – 0.1 wt % in 70% ethanol.

Methyl red indicator solution – 0.1 wt % in deionized water.

All water used should be deionized or distilled and boiled to be carbon dioxide free. If the presence of carbon dioxide is suspected, a blank determination should be made.

Procedure: Pipette 50 **mL** of the water or brine sample into a 250 **mL** beaker

and add a few drops of phenolphthalein indicator.   If a pink

color is evident, titrate with standard **HCl** until a clear endpoint

is reached.   Add a few drops of methyl red indicator and titrate

to the bright pink methyl red endpoint.   Usually 0.1 N **HCl** is

used but 0.01 N **HCl** should be used if the titer with 0.1 N is

unusually small.   Save the acidified solutions for gravimetric

determination of sulfate.

Calculations: There are three possible cases for alkalinity in mineral waters.

The first case is the presence of only hydroxyl and carbonate

species, the second is the presence of carbonate only, and the

third is the presence of both carbonate and bicarbonate. In

order to distinguish the three cases, it is important to compare

the titration to the phenolphthalein endpoint with the titration

from the phenolphthalein endpoint to the methyl red endpoint.

For convenience, the volume of **HCl** needed to titrate to the

phenolphthalein endpoint will be called P and the volume of **HCl**

needed to titrate from the phenolphthalein endpoint to the methyl

red endpoint will be called **M.**   Both P and M are in units of **mL.**

N = normality of the **HCl** solution.

Case 1.   P is greater than **M.**

$(P-M)xNx(17 \text{ mg/meq})(20) =$ hydroxyl concentration in

µg OH-/mL

$(MxN)x(60 \text{ mg/meq})(20) =$ carbonate concentration expressed

µg $CO_3^=$/mL

Case 2.   P = M

$PxNx(60 \text{ mg/meq})(20) =$ carbonate concentration in

µg $CO_3^=$/mL

45

Case 3. P is less than **M.**

$$P \times N \times (60 \text{ mg/meq})(20) = \text{carbonate concentration in}$$
$$\mu g \ CO_3^=/mL$$

$$(M-P) \times N \times (60 \text{ mg/meq}) \times (20) = \text{bicarbonate concentration in}$$
$$\mu g \ HCO_3^-/mL$$

Note 1. To find **weight** percentages of the above constituents.in the original
salt core before dissolution, multiply the above results by 0.05 and
divide by the weight of the salt sample in grams. This assumes the
solution containing the dissolved salt was diluted to 500 **mL.**

Note 2. A blank determination of the alkalinity should be performed on the
water used to dissolve the salt core, and the results of the blank
should be subtracted from the sample **alkalinity.**

Sulfate

Scope: This method is used to determine the sulfate content of various mineral
waters by means of a gravimetric precipitation technique.

Reference: J. S. Fritz and **G. H.** Schenk, Jr., <u>Quantitative Analytical Chemistry</u>.
Boston, MA. Allyn bacon, Inc., 1966.

Apparatus: Filter crucibles with approximately eight micron pore size (Berlin
type **1A3** work well for this).
Standard laboratory muffle furnace.
Usual laboratory glassware. Volumetric glassware Class A or equivalent.

Reagents: Analytical Reagent grade barium chloride, aqueous solution, 10%
by **weight.** All water used was deionized.

Procedure: Heat the solutions from the alkalinity determinations to near boiling.
Stir each solution constantly while slowly adding approximately 5 **mL**
of hot 10% barium chloride solution. Cover the solutions and keep

them near boiling for an additional hour. Remove solutions from heat and let stand-covered overnight. Filter the solutions through prefired and tared filter crucibles using suction. Police the sample beakers carefully and rinse into the crucibles. Wash the precipitates thoroughly with hot water and fire the crucibles at **750°C** for one hour. Cool the crucibles and reweigh.

Calculations:

$$\frac{(\text{weight } BaSO_4)(0.41158)(100)(10)}{(\text{weight sample dissolved in 500 mL})} = \text{weight percent } SO_4^=$$

0.41158 = gravimetric factor
10 = volumetric factor
100 = converts weight fraction to percentage

Chloride

Scope: This method is used to determine the chloride content of various mineral waters by means of a precipitation titration with silver nitrate according to Fajans.

Reference: **J. S.** Fritz and **G. H.** Schenk, Jr., <u>Quantitative Analytical Chemistry</u>. Boston, MA. **Allyn** Bacon, Inc. 1966.

Apparatus: Usual laboratory glassware. Volumetric glassware Class A or equivalent.

Reagents: All reagents are " analytical reagent" grade.

0.1 N silver nitrate accurately standardized against dry sodium chloride.

Dichlorofluorescein indicator - 0.1% dichlorofluorescein in 70% ethanol. (Eastman **2',7'-Dichlorofluorescein)**.

All water used was deionized.

Procedure: Pipette 10 **mL** of each of the SPR solutions to separate 100 **mL** volumetric flasks. Dilute to mark. Transfer a'10 **mL** aliquot of

this diluted sample into a 250 **mL** Erlenmeyer flask and add approx.
100 **mL** of deionized water. Add 5 drops of dichlorofluorescein
indicator and titrate with standard silver nitrate with constant
swirling until the appearance of a pink color.

Calculations:

$$\frac{(mL\ AgNO_3)(normality\ AgNO_3)(35.453\ mg/meq)(500)(100)}{(weight\ of\ sample\ dissolved\ in\ 500\ \textbf{mL})(1000)} = weight\ percent\ Cl^-\ in\ core$$

35.453 = mg Cl/meq Cl
  500 = dilution factor
  100 = converts **weight** fraction to wt %
 1000 = converts g to mg

Calcium and Magnesium

Scope: This method is used to determine the calcium and magnesium content of
various mineral waters.

Outline of Procedure: Samples of SPR solutions are titrated with standard
EDTA solution using two different indicators. Titration to the
Erichrome Black T endpoint gives the sum of the Ca plus Mg. Titration
to the murexide endpoint gives only the **Ca. Mg** is calculated from
the difference between the two titrations.

Reference: J. S. Fritz and G. H. Schenk, Jr. Quantitative Analytical Chemistry.
Boston, MA. Allyn and Bacon, Inc. 1966.

Apparatus: Usual laboratory glassware. Volumetric glassware-Class A or equivalent

Reagents: All reagents are "analytical reagent" grade.
Potassium hydroxide pellets.
Murexide indicator, undiluted powder.
Buffer solution — 60 g ammonium chloride in 200 **mL** deionized water
plus 570 **mL** concentrated ammonium hydroxide all diluted to 1000 **mL**
with deionized water.

Eriochrome Black T indicator, undiluted powder.

0.01 M EDTA solution — EDTA disodium salt in deionized water. Accurately standardized against Mallinckrodt primary standard calcium carbonate.

All water used was deionized.

Procedure: Quantitatively transfer 20 **mL** aliquots of the SPR solution into two separate 125 **mL** Erlenmeyer flasks. Add approximately 20 **mL** of deionized water to each flask. To the first flask add 4 KOH **pellets** and a small amount of murexide indicator. Using the standard-ized EDTA solution, titrate to the violet endpoint. Introduce 5 **mL** of buffer into the second flask. Add a small amount of **Erio-**chrome Black T indicator and titrate to the blue endpoint with standardized EDTA.

Calculations:

$$\text{Wt \% Ca}^{++} = \frac{(M)(A)(40.08)(25)(100)}{(1000)(\text{weight sample dissolved in 500 \textbf{mL}})}$$

$$\text{Wt \% Mg}^{++} = \frac{(M)(B-A)(24.31(25)(100)}{(1000)(\text{weight sample dissolved in 500 \textbf{mL}})}$$

A = **mL** EDTA to murexide endpoint
B = **mL** EDTA to Eriochrome Black T endpoint
M = molarity of standard EDTA solution
40.08 = grams Ca per mole Ca
24.31 = grams Mg per mole Mg
25 = dilution factor
100 = converts weight fraction to wt %
1000 = converts liters to milliliters

Atomic Absorption

The stock brine contains about 100 g of core dissolved in 500 **mL** solution. Make **1/10, 1/100** and **1/1000** dilutions of each solution to be analyzed. Each dilution should contain 1000 **mg/L** Cs ionization buffer. Cs is added as a Cl solution.

<u>Standard Preparation</u>:   Prepare four volumetric flasks to contain 0, 50, 75,

and 100 **mg/L** Na.   Add **CsCl** solution so that each flask contains 1000 **mg/L**

Cs when diluted to volume with deionized water. Prepare four more volu-

metric flasks to contain the following concentrations:

K	0	5	10	15	**mg/L**
Ca	0	2.5	5	10	**mg/L**
Mg	0	1	3	5	**mg/L**

Each standard should also contain 1000 **mg/L** Cs when diluted with deionized

water.

<u>Sample analysis</u>:   Analyses run on Varian AA-6.

Standardize for Na analysis using a wavelength of 330.2 **nm,** a spectral

bandpass of 0.2 nm and an air-acetylene flame.   Analyze the **1/1000** dilutions.

Standardize for K analysis using a wavelength of 769.9 **nm,** a spectral

bandpass of 0.5 nm and an air-acetylene flame with the burner rotated about

30°.   Analyze the **1/10** dilutions.

Standardize for Mg analysis using a wavelength of 285.2 nm, a spectral

bandpass of 0.5 nm and an air-acetylene flame with the burner rotated about

45°.   Analyze the **1/10** dilutions.

Standardize for Ca analysis using a wavelength of 422.7 nm, a spectral

bandpass of 0.5 nm and nitrous oxide-acetylene flame with the burner rotated

about **15°.**   Analyze the **1/100** sample dilutions.

Please note that wavelength, flame stoichiometry and burner orienta-

tion are optimized for each element analyzed.

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